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KINETIC STUDY OF THE CATALYTIC EFFECT OF ZINC(II) ION ON THE DEHYDROGENATION OF ATACTIC POLYPROPYLENE BY SULFUR

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ABSTRACT

The influence of zinc stearate on the dehydrogenation of atactic polypropylene (APP) by sulfur has been studied by thermal differential analysis. The stearate is quickly converted into ZnS which then reacts with the biradicals S_8 , giving a polysulfide, which dehydrogenates APP, this process being catalyzed by ZnS. A reaction sequence for the overall process is proposed.

INTRODUCTION

While atactic polypropylene (APP) dehydrogenation by sulfur has been shown to give a polyunsaturated product of some practical use, the very slow reaction rate of this process [1] precludes its industrial application. Since amines have been proved to be unsatisfactory as catalysts for this process [2], and free-radical activation presents many difficulties in its application [3, 4], we decided to study an alternative way to accelerate the reaction by using heavy metal ions and, among these, Zn(II) seems to be the most likely to be effective, in view of its action in vulcanizing systems.

The only relevant information available is the series of works of Dogadkin et al. [5-10] on polyethylene, which seem to indicate that, in addition to unsaturation, sulfur compounds and crosslinks can also be formed in

the process. Thus, it was decided to study the reaction between APP and sulfur in the presence of Zn(II) (added as stearate to ensure its solubility in the reaction mass) in bulk, by differential scanning calorimetry.

EXPERIMENTAL PROCEDURE AND REAGENTS

The APP used was TAQSA's "U" quality, with \bar{M}_n 8000. It was purified by steam distillation, followed by washing to remove catalyst residues and by heating to 270°C at 40 torr for 2 h. Its IR spectra were identical with those given in Ref. 11, apart from a much lower level of residual oxidation. Its tacticity determined by NMR was entirely random (average sequence lengths: isotactic 1.31, syndiotactic 1.33). The sulfur was from Erba, reagent grade, and the zinc(II) stearate was from Merck, both being used as received.

Samples of APP-sulfur mixtures in proportions varying between 0.15 and 0.20 mol sulfur/mol APP, and also between 3 and 11 mol sulfur/mol APP, were placed in a cup, put into a Mettler TA3000 DSC, and heated under nitrogen to a temperature in the 120–210°C range, the amount of heat evolved being then plotted against time. Dynamic determinations were also tried, but the complexity of the process precluded their use. Samples containing an excess of sulfur gave, in general, less reproducible results than those with an APP excess, and they were not used to calculate kinetic parameters.

RESULTS AND DISCUSSION

The isothermal thermograms show the characteristic S-form of a successive reaction mechanism (see Fig. 1). Powell treatment of samples with excess APP shows a behavior corresponding to a two-step first-order/zero-order successive mechanism, while when sulfur is in excess, the process is zero-order/first-order (see Fig. 2). In both cases, at very low reaction times, the process shows no definite reaction order. This can be attributed to the fact that, in the initial stages of the process, zinc stearate is converted quickly into zinc sulfide by the hydrogen sulfide produced in the dehydrogenation (as determined by Dontsov [8] in similar circumstances), and the heat evolved distorts the thermograms. Thus, the sulfide can be considered to be the species responsible for the catalytic effect.

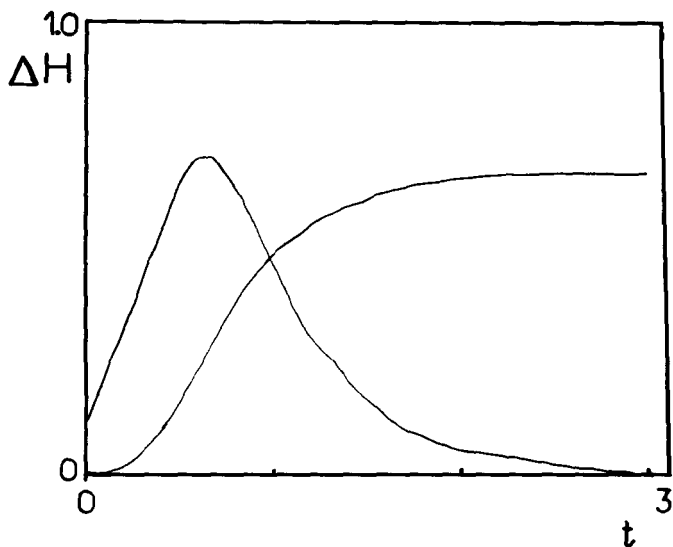


FIG. 1. A typical heat vs time plot for the reaction APP-S in the presence of $ZnSt_2$ (lower curve is the derivative, not to the same scale).

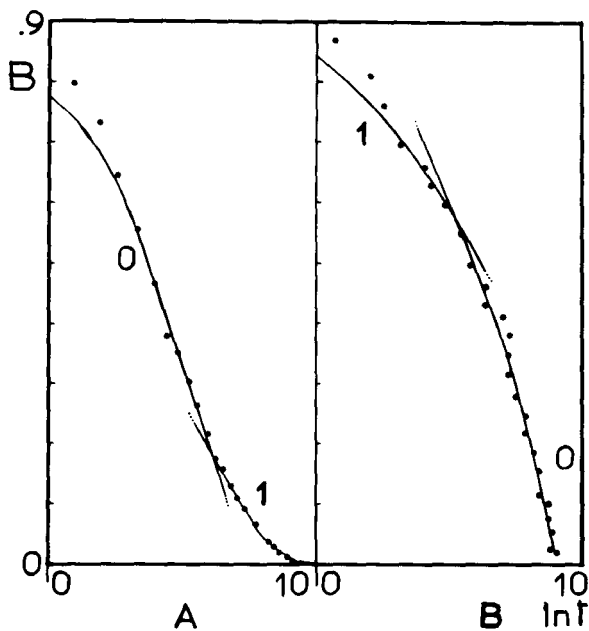
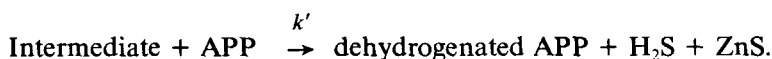
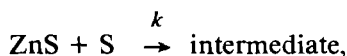


FIG. 2. Powell plots for the reaction between APP and sulfur carried out in the presence of an excess of the former (A) or of the latter (B) at $210^\circ C$ with $1.84 \text{ mol } ZnSt_2/100 \text{ kmol APP}$. Curves corresponding to the different reaction orders are superimposed (continuous lines).

The IR spectra of the treated polymer differ from those of APP only in showing peaks attributable to the presence of trisubstituted *trans* double bonds, being in fact identical to those found when the reaction is carried out in the absence of catalyst [1] or when aniline is added [2]. Also, hydrogen sulfide was the only detectable gaseous product. From these data it can be assumed that the phenomenological overall process can be described by the reactions



For a successive mechanism of this type when the process is carried out in the presence of an excess of APP, the rate law for heat evolution will be

$$d(H)/dt = k([\text{S}]_0 \Delta H_r - \Delta H + \Delta H_r' k' t) + \Delta H_r' k', \quad (1)$$

where $[\text{S}]_0$ is the initial sulfur concentration, ΔH is the total enthalpy variation at time t , and k , k' , ΔH_r , and $\Delta H_r'$ are the rate constants and reaction enthalpies corresponding to the first and second steps. Also, the total reaction enthalpy $\Delta H_{r(T)}$ is

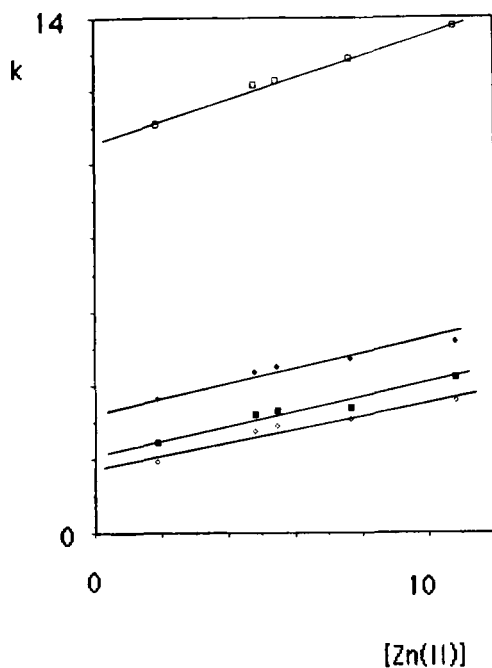
$$\Delta H_{r(T)} = \Delta H_r + \Delta H_r' \quad (2)$$

Since $\Delta H_{r(T)}$ has to have the same value as that for the uncatalyzed process, which can be calculated from data in Ref. 12, the values of k , k' , and ΔH_r were determined from the experimental data t , ΔH and dH/dt , at different temperatures and catalyst concentrations, from Eqs. (1) and (2), by means of a minimax nonlinear optimization subroutine developed by Madsen [13] and Schaër-Jacobsen [14], all calculations being carried out by computer.

As it can be seen from the results in Table 1, both rate constants are strongly dependent on [zinc(II)], both dependences being linear ones (see Figs. 3 and 4). From the experimental behavior, it can be concluded that it takes place via two successive, nonelementary steps, the first one giving an S-Zn intermediate, which then reacts with APP to give dehydrogenated APP and H_2S . Both processes will be studied separately.

TABLE 1. Pseudo-First-Order Rate Constants k and k' ^a for the Reaction between APP and S^b in the Presence of Zinc Stearate

Zinc stearate ^c	120°C		150°C		180°C		210°C	
	k	k'	k	k'	k	k'	k	k'
1.84	11.1	101	3.65	151	2.47	242	1.93	379
4.79	12.2	105	4.33	167	3.21	273	2.73	391
5.46	12.3	110	4.50	173	3.30	275	2.90	403
7.65	12.9	120	4.69	180	3.40	286	3.07	417
10.8	13.8	155	5.17	192	4.20	304	3.56	442

^aIn (ks)⁻¹.^b[APP]/[S] = 0.0592.^cIn mmol ZnSt₂/10 mol APP.FIG. 3. Dependence of k (in 1/ks) on Zn(II) concentration (in mol/10 kmol APP) at (top to bottom) 120, 150, 180, and 210°C.

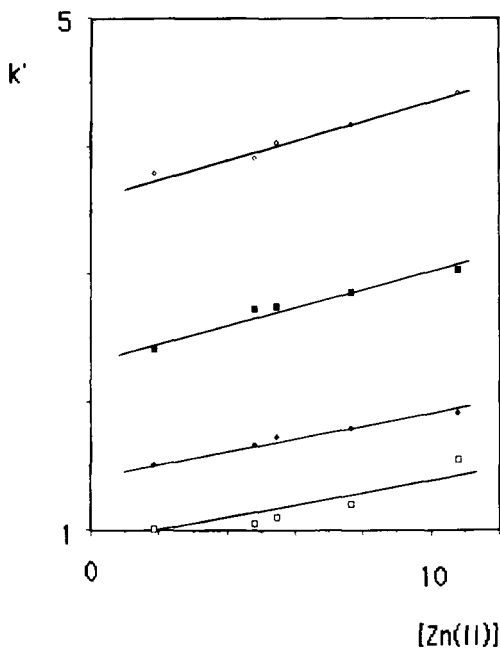
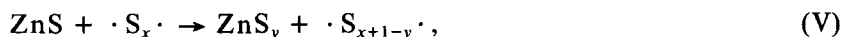


FIG. 4. Dependence of k' (in 1/100 ks) on Zn(II) concentration (in mol/10 kmol APP) at (top to bottom) 120, 150, 180, and 210°C.

Before trying to interpret intermediate formation, it is convenient to remember that, in the temperature range studied, there exist two main stable forms of sulfur: S_8 rings and radical-ended polymeric chains (the proportion of S_7 rings being very small) [15], the latter reaching a maximum of 45 wt% at 162°C [16]. Thus, there are two forms capable of reaction in our temperature range. Since there is no information available about the reaction between S and ZnS, it is difficult to define the nature of the intermediate from the available data, but the value of the calculated enthalpy change for the first step (average $\Delta H = 9.73$ kJ/mol) seems to preclude its being a radical species such as the $\cdot S_8 \cdot$ biradical. Moreover, the ordinates of the k vs $[Zn(II)]$ plot, i.e., the rate constants for uncatalyzed intermediate formation, are very different from the corresponding ones calculated for the uncatalyzed dehydrogenation (see Ref. 1), thus confirming that the intermediate is not the same in both cases. Thus it

seems better to assume that the intermediate is a ZnS compound. The possibility of its being a pyrite-type dichalogenid is slight in view of their thermal stability [17, 18], while different zinc polysulfides ranging from $\text{ZnS}_{1.70}$ to $\text{ZnS}_{3.25}$ have been prepared, with possibilities of existence for species having more than five S-atoms per molecule [19]. Thus it seems reasonable to consider that the intermediate is a zinc polysulfide, although no definite formula can be given. The following reaction sequence is proposed for intermediate formation:



where the minimum value of y is 2. Then, applying the steady-state approximation to the S_8 biradical (a short-lived species), the rate law for intermediate formation would be

$$d[\text{ZnS}_y]/dt = K_1(k_2 - k_3) + k_3[\text{S}] + k_5([\text{S}] - K_1)[\text{ZnS}] \quad (3)$$

This expression satisfies the observed kinetic behavior. K_1 can be determined from Eyring's data [20]. From the experimental rate constants, together with data obtained previously for the uncatalyzed process [1], the values of k_2 , k_3 , and k_5 can be obtained by Eq. (3). These kinetic constants satisfy both the Arrhenius equation and the transition state theory, and their activation parameters are given in Table 2.

These results deserve some comments. The relatively high difference between the values of the activation energies corresponding to S-chain breaking (Reaction II) and S-ring opening (Reaction III) could mean that the S_8 biradical has a nonlinear structure and that the activated complex lies closer to it than to the products having a structure more akin to the ring than to the chain. While the preexponential factor for Reaction (II) is of the order of magnitude predicted by the transition state theory [21] for unimolecular processes, that for S-ring opening (Reaction III) is much lower, which can be justified on the basis that the S_8 biradical is in a low-

TABLE 2. Activation Parameters for Reactions (II), (III), and (V) in an APP-S Melt

Reaction	E_a , kJ/mol	A	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , kJ/(mol · K)
II	107.0	2.52 ^a	111.0	0.0987
III	66.0	4.50 ^b	69.6	-0.0113
V	2.6	1400 ^c	6.2	-0.0401

^aIn (ps)⁻¹.^bIn (ms)⁻¹.^cIn L/(mol · ms).

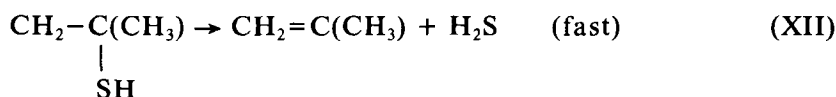
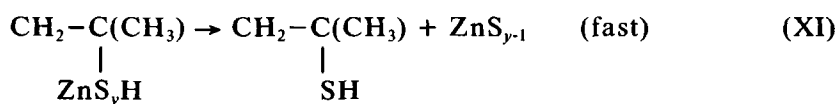
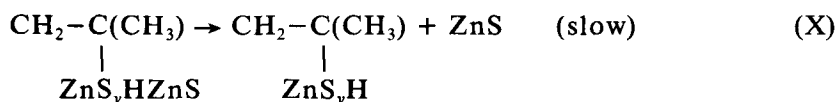
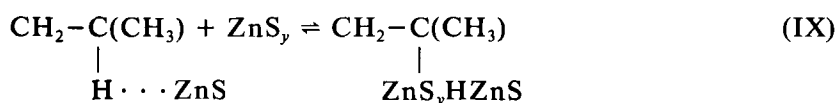
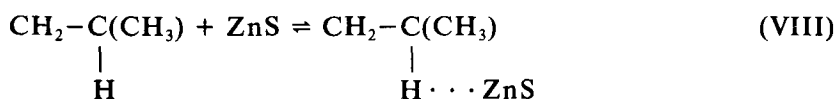
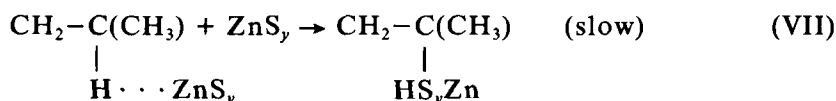
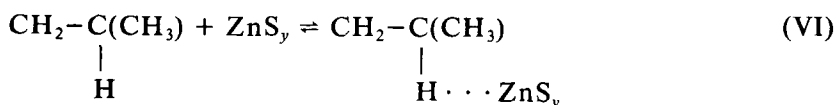
lying triplet state, while the ring is a singlet. Thus ring opening on activation entails a crossing, and single-triplet transitions have a low probability in molecules composed only of relatively light atoms, such as sulfur.

The preexponential factor value for Reaction (V) is very much like that predicted by the T.S.T. for a nonlinear ring formation by two linear reactants on activation [21], and thus gives some support to our hypothesis about the nature of the reaction intermediate, zinc polysulfides having a cyclic structure.

The reduction in the number of molecules present on activation in Reaction (V) justifies the negative value of its activation entropy, while the positive one found for Reaction (II) confirms that the activation entails an increase in chain freedom, which can be due to the fact that the end-chain S-atom (a radical) is folded back, so that the empty *d* orbitals in the next-to-last S-atom can stabilize the radical. Such a structure would require a fair amount of energy to be destroyed on activation.

In the reaction between ZnS_{*n*} and APP, we can see that there is also a linear dependence of the rate constant on [ZnS], which can only mean that the reaction between APP and zinc polysulfide is catalyzed by ZnS, a molecule having a strong ionic character ($\Delta H_{(\text{dissoc})} = 205$ kJ/mol [22]), and which can therefore promote strong dipole-induced dipole interactions. The rate constants for the uncatalyzed process are on the order of 0.01 mL/(s · mol), a rather low value. It is plausible then to think that the catalytic effect takes place via an association between the ZnS molecule and the tertiary H atom, which already has a slight acidic character, weakening the C-H bond. This association can consist in the formation of an H-bond between H and S. While the uncatalyzed process can also begin with the formation of an APP-ZnS_{*n*} adduct via a similar bond, such a process ought to be much slower, due both to the steric impediment caused by the relatively big size of the polysulfide molecule (an effect that

will be enhanced by the closeness of the adjacent methyl groups in the APP syndiotactic triads) and to the fact that the polysulfide has a much more uniform charge distribution than the ZnS. The following reaction sequence is proposed, based on the above considerations.



where Steps (VI) and (VII) correspond to the uncatalyzed adduct formation, Steps (VIII)–(X) represent the catalyzed formation and (XI) and (XII) are thiol formation and decomposition.

The kinetic rate law for adduct formation (the rate-determining step) for this sequence will be

$$\begin{aligned} d[\text{APPZnS}_y]/dt &= K_6k_7[\text{APP}][\text{ZnS}_y] \\ &+ K_8K_9k_{10}[\text{APP}][\text{ZnS}_y][\text{ZnS}]. \end{aligned} \quad (4)$$

This is consistent with experimental results, but very little can be learned about the different steps from it. A very rough estimation based on the slope of the Arrhenius plot for the experimental rate constant k' (which in this case will correspond to the sum of the reaction enthalpy of Reaction (VI) and the activation energy of Reaction (VII) and the average values for H– and C–S bond energies [23, 24]) gives for the uncatalyzed adduct formation, Reaction (VIII), an activation energy of some 253 kJ/mol, whereas the same treatment gives a value of only 107 kJ/mol for its catalyzed formation (IX). While these values are very imprecise, they can give some idea about the magnitude of the steric impediment to the direct reaction between APP and zinc polysulfide, compared to the catalyzed process. In fact, this rules out any possibility of carrying out APP dehydrogenation by treatment with zinc polysulfides on an industrial scale.

CONCLUSIONS

In the light of the results obtained, it is concluded that the presence of zinc sulfide significantly accelerates dehydrogenation of APP by sulfur, that only dehydrogenation takes place under these experimental conditions, and, therefore, that this process could be industrially worthwhile.

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